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A generalized model for the structural investigation of liquid Li_4Pb

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Abstract : A generalized model for partial structure factors of charged-hard-sphere mixture of arbitrary charge and size is employed for the structural investigation of liquid Li-Pb in stoichiometric composition, treating the sample as partially charge transfer system. The computed concentration – concentration structure factor $S_{cc}(k)$ is compared with experimental results. The overall agreement between theoretical and experimental structure factors is satisfactory.

Keywords : Stoichiometric composition, partial structure factors, Mean spherical model approximation, direct correlation function, Percus-Yevic approximation

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1. Introduction

In recent years, structural investigations of liquid alloys were extended to systems showing some peculiar structural properties [1, 2]. These can be divided into two groups : (i) The first group exhibits some short range order due to compound forming nature such as Mg-Sn, Li-Pb, Na-Pb and Na-Sn [3, 4-7]. (ii) The second group shows a tendency to segregation such as Al-Sn, Al-In, Na-Li and Cu-Bi [1, 5, 8, 9].

It may be stated that liquid alloys Li-Pb and Na-Pb *etc* do not necessarily form a simple alloy though they are formed of two simple metals. The Liquid Li-Pb is an important and well studied binary metallic fluid which shows highly pronounced deviations from ideal mixing behaviour at particular composition.

The measured thermodynamic, electrical and magnetic properties, the Knight shift and spin-lattice relaxation time, all show marked deviations from ideality at concentrations close to the composition Li_4Pb [4].

Many authors have attempted to account for various properties of Li_4Pb in terms of formation of chemical complexes with finite life times. However, direct evidence for the existence of chemical complexes in Li-Pb has not emerged. Indeed, many experiments indicate that there is pronounced charge-transfer (electron) from Li atoms to Pb in this alloy around stoichiometric composition. The present work is based on the second line of approach.

On the other hand, a model for partial structure factors is worked out through the Blum's formalism of direct correlation functions for assymetric charged-hard-sphere mixtures for most general case of arbitrary charge and size in the primitive model of electrolytes under Mean Spherical Model Approximation (MSMA) and it is conveniently simplified for 1-1 systems [10] and applied in the molten salts (RbCl, Rb-Br) [11] and strongly ionic melts Cs-Au [12].

Hence, author felt the need to test the validity of the model in the systems which are not fully ionic *i.e.* partial charge transfer takes place and Li-Pb is one of the such suitable system in and around stoichiometric composition.

2. Method

In this section, general steps of the model will be discussed as the details of the expressions can not be presented here.

2.1. Direct correlation function :

According to the Blum's formalism of $C_{ij}(r)$, the direct correlation function between i-th and j-th type of ions, can be concisely written as :

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$$C_{ij}(r) \begin{cases} = C_{ij}^0(r) - \alpha_{ij} & \text{in the region } 0 \le r < \lambda_{ij} = (\sigma_j - \sigma_i)/2 \\ & \text{when } \sigma_i < \sigma_j, \\ = C_{ij}^0(r) + \dfrac{e^2}{\varepsilon_0 k_B T}\left[\dfrac{P_{ij}}{r} + Q_{ij} + R_{ij} r + T_{ij} r^3\right] & \\ & \text{for } \lambda_{ij} \le r < \sigma_{ij}, \text{ when } \sigma_i < \sigma_j \\ \dfrac{Z_i Z_j}{\varepsilon_0 k_B T}\dfrac{e^2}{r} & \text{for } r > \sigma_{ij}. \end{cases} \quad (1)$$

Here, $\sigma_i \Rightarrow$ diameter of the species i,

$\varepsilon_0 \Rightarrow$ dielectric constant of the medium,

$T \Rightarrow$ Temperature of the melt,

$e \Rightarrow$ Charge of the electron,

$Z_i \Rightarrow$ amount of charge in electron unit in the i-th ion.

The other symbols have given and explained fully in the previous works [10-12]. Here, $C_{ij}^0(r)$'s are the direct correlation functions for a mixture of neutral hard sphere in the Percus-Yevic approximation and given a general form by Hiroike for n-component system and this can be concisely written as follows:

$$-C_{ii}^0(r) = a_i + b_i r + d r^3 \quad \text{for } r < \sigma_i, \quad (2a)$$

$$-C_{ij}^0(r) = \begin{cases} a_i & \text{for } r < \lambda_{ij}, \\ a_{ij} + b_{ij} r + d r^3 + (f_{ij}/r) & \text{for } \lambda_{ij} < r < \sigma_{ij}, \end{cases} \quad (2b)$$

where

$$C_{ij}(r) = C_{ji}(r), \ \sigma_{ij} = (\sigma_i + \sigma_j)/2, \ \lambda_{ij} = (\sigma_j - \sigma_i)/2,$$

$$a_{ij} = (a_i + a_j)/2 \text{ and } b_{ij} = (b_i + b_j)/2.$$

Here, a_i, b_i, d and f_{ij} can be identified in explicit form in Hiroike's fomalism [13] and can be simplified in a convenient working form for the systems of interest.

Here, it also should be stated that $\alpha_{ij}, P_{ij}, Q_{ij}$ and T_{ij}, R_{ij} of eq. (1) are functions of a Γ-scaling parameter.

The Γ-parameter is related by a rational expression.

$$\Gamma^2 = \frac{\pi e^2}{\varepsilon_0 k_B T} D(\Gamma). \quad (3)$$

The details of the function $D(\Gamma)$ have been explained in the earlier works [10, 14] and Γ-can be solved numerically as already discussed [10]. It is found that Γ-parameter is analogous to Debye inverse screening length and may be termed as generalized Debye inverse screening length parameter for a mixture of arbitrary charge and size. Also it should be stated that Γ is a very sensitive parameter in the determination of structure factors.

Using eqs. (1), (2a) and (2b) the Fourier Transformations can be obtained in a straight forward way even though it is cumbersome. A convenient form for 1-1 system has been given in earlier works [10, 12].

2.2. *Partial and total structure factors :*

As it is well known that partial structure factors $S_{ij}(k)$ and $C_{ij}(k)$, the partial direct correlation functions in k-space is related in the following matrix form:

$$\tilde{S}(k) = (\mathbf{1} - \tilde{C}(k))^{-} \quad (4)$$

The partial structure factor $S_{ij}(k)$ is an (i, j) component of the inverse matrix $(\mathbf{1} - \tilde{C}(k))^{-1}$ and $\tilde{C}_{ij}(k)$ is given by

$$\tilde{C}_{ij}(k) = \sqrt{\rho_i \rho_j} \int dr \; C_{ij}(r) \exp(i\mathbf{k}.\mathbf{r}). \quad (5)$$

The coherent scattering intensity $I(k)$ can be written in terms of the partial structure factors as

$$I(k) = N \sum_{i=1}^{n} \sum_{j=1}^{n} \sqrt{c_i c_j} f_i(k) f_j(k) S_{ij}(k), \quad (6)$$

$f_i(k) \Rightarrow$ atomic scattering factor depends on k for X-ray and electron diffraction while for neutron diffraction, it is a scattering amplitude which does not depend on k. c_i is the atomic fraction of i-th species.

Eq. (6) can be written in the short wave length limit as follows:

$$I(k \to \alpha) = N \sum^{n} c_i f_i^2(k)$$

$$= N < f^2(k) >,$$

as $$S_{ij}(k \to \alpha) = \delta_{ij}. \quad (7)$$

Hence, total structure factor $S(k) = I(k)/I(k \to \alpha)$

$$= \sum_{i=1}^{n} \sum_{j=1}^{n} \sqrt{c_i c_j} \frac{f_i(k) f_j(k)}{< f^2(k) >} S_{ij}(k). \quad (8)$$

3. Results and discussion

At the stoichiometric composition *i.e.* in Li_4Pb, the average value of the scattering length is very close to zero so that a single neutron diffraction experiment yields the concentration structure factor $S_{cc}(k)$ and is related to the partial structure factors as follows:

$$S_{cc}(k) = c_1 c_2 (c_2 S_{11}(k) + c_1 S_{22}(k) - 2(c_1 c_2)^{1/2} S_{12}(k)). \quad (9)$$

Here, 1 stands for Li atom and 2 for Pb atom while c_1 and c_2 are

their atomic fractions. $S_{cc}(k)$ is a measure of the concentration fluctuation at a wave vector k, it provides direct information about chemical short range order in the alloy and reflects the character of the bonding. Ruppersberg and Reiter [4] found pronounced chemical ordering effects in Li_4Pb [4].

Hence, the present model computation is based on the following physically acceptable assumption.

(i) pronounced charge transfer takes place from *Li* atoms to *Pb* atoms in and around stoichiometric composition, maintaining the charge conservation condition.

$$c_{Li}\,\Delta Z_{Li} + c_{Pb}\Delta Z_{Pb} = 0 \qquad (10)$$

and *Li* atom become effectively charged positive ions while Pb atoms are effectively charged negative ions.

(ii) Along with the other cases [15], the dielectric constant is taken to be unity.

The input data is given in Table 1. Here, for uniformity of the notations, σ_{ii}'s are written for σ_i, and these values are very close to Pauling's diameters ($\sigma_{Li} = 2.50$ Å & $\sigma_{Pb} = 3.00$ Å) though they are slightly adjusted to obtain best fitted experimental structure factors S(k) = $S_{cc}(k)/c_1c_2$ and it is obvious that the values of σ_{ii}'s of pure metals should change with composition of the alloy. The density (ρ =0.04601 Å^{-3}) of the melt at 995°K is taken from literature [16].

Table 1. Input data and potential parameters

Temperature	Density*	Diameters(Å)		Computed	Effective charge	
T(°K)	ρ(Å^{-3})	$\sigma_{Li\,Li}$	$\sigma_{Pb\,Pb}$	Γ (Å^{-1})	ΔZ_{Li}	ΔZ_{Pb}
955	0.04601	2.50	3.00	0.715	+0.218	-0.872

* The experimental values of the density is taken from literature [16]

The exact values of ΔZ_i's are obtained through the computer scanning and it is found that $\Delta Z_{Li} = +0.218$ and $\Delta Z_{Pb} = -4\Delta Z_{Li} = -0.872$ correspond to the best fitted theoretical results in comparison with experimental structural data [4]. The generalized screening length parameter Γ is calculated in our usual method and the value is obtained 0.715 Å^{-1}.

Figure 1 shows the comparison of theoretical results with the experimental structure factors $S_{cc}(k)/c_1c_2$. The overall agreement between the computed theoretical structure factor and experimental values is satisfactory though there is a small deviation in the second peak region. The theoretical main peak height is excellently matched with experimental height but the position is slightly shifted towards the low k value. The theoretical main peak of $S_{cc}(k)$ at $k \approx 1.5$ Å^{-1} whereas experimental main peak lies close to $k \approx 1.53$ Å^{-1}. Hence, Figure 1 depicts that the theoretical curve around the main peak is very slightly lagging behind the experimental curve.

The partial structure factors $S_{ij}(k)$ corresponding to these results are shown in Figure 2. $S_{Pb\text{-}Pb}(k)$ exhibits its main maximum

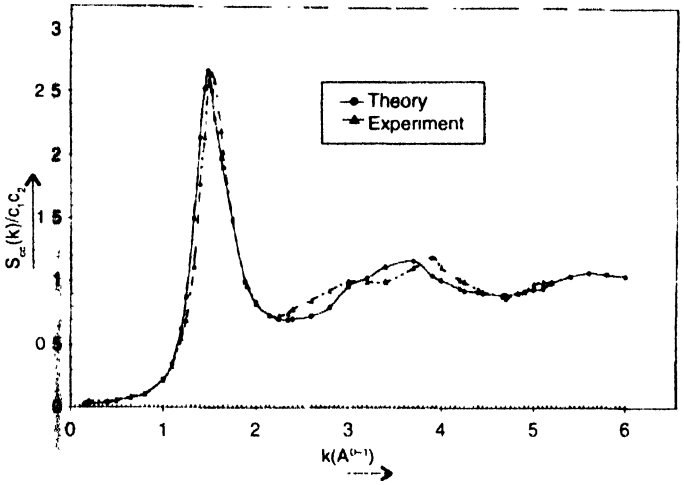

Figure 1. The computed structure factors $S_{cc}(k)/c_1c_2$ (• • •) is compared with experimental results (-▲-▲-▲).

at $k = 1.5$ Å^{-1} whilist $S_{Li\text{-}Li}$ has a weak maximum and $S_{Li\text{-}Pb}(k)$ has a deep minimum at the same wave vector $S_{Li\,Li}(k)$ and $S_{Li\,Pb}(k)$ show their maximum at $k \approx 2.55$ Å^{-1} while $S_{Pb\text{-}Pb}(k)$ has the weak maximum at the same position. However, the pattern of the present computed partial structure factors conforms with the pattern as calculated by Copestake *et al* [17] using ordering potential which they have extracted from experimental $S_{cc}(k)$.

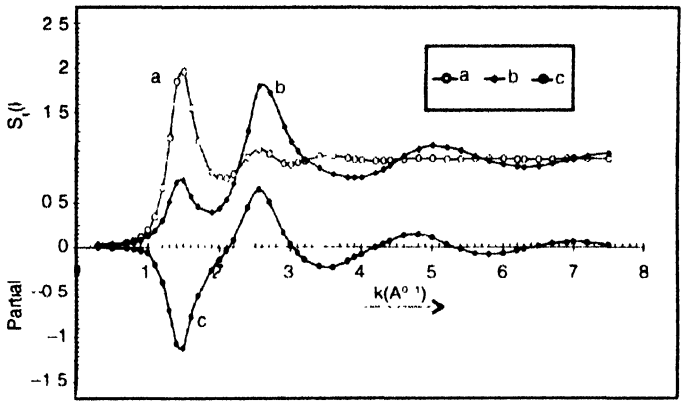

Figure 2. The partial structure factors $S_{Pb\,Pb}(k)$ (-o-o-), $S_{Li\,Li}(k)$ (-◆-◆-) and $S_{Li\,Pb}(k)$ (-•-•-) computed in the present model at 955°K

However, in summary of the present fluctuation results it may be stated that Li_4Pb at 995°K can be modelled realistically by coulomb potentials with effective electron charges of + 0.218 on a Li atom and -0.872 ($-4\Delta Z_{Li}$) on a Pb atom, and generalized inverse screening length of 0.715 Å^{-1} which is automatically determined by the diameters (σ_{ii}'s), charges (ΔZi's) and number densities (ρ_i's) of the species.

Here, it should be stated that it is difficult to formulate a reliable relation between the partial ionic character and the difference in electronegativity of the two atoms between which

the charge transfer taken place. But, through the Pauling's empirical formula a curve between ionic character *vs* electronegativity difference shows 15 percent ionic nature in a single bond between the two atoms having 0.8 electronegativity difference as in the present sample. Hence, the present computer scan data for effective charges of the atom is also be apparently supported by Pauling's point of view [18].

4. Conclusion

The computed structural results of Li-Pb provides confidence to undertake the investigations on few more partially charge transfer systems' (like Na-Pb, Na-Sn *etc*) using this generalized model. It may be concluded that this model not only works very well on the molten salts, strongly ionic melts (like Cs-Au *etc*) but also it is satisfactorily working on the partially charge transfer sample.

Here, it should be stated that the very important significance of this model is that it does not contain any unknown unphysical parameters like Waisman – Lebowitz solution [19, 20] for a mixture of ionic fluids of asymmetric nature (unequal radii) which contains seven unknown parameters for obtaining partial structure factors and these are connected through the seven complicated equations. [21].

In this model, generalized screening length parameter Γ is determined by diameters (σ_i's), number densities (ρ_i's) and charges (ΔZ_i's) of the species. The diameters are usually found close to Pauling's or Fumi-Toshi values.

The model is generalized in the sense that it is applicable to the ionic mixture of asymmetric diameters (unequal radii) and arbitrary charges of the species in the evaluation of partial and total structure factors.

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